Comparison of activated fly ash carbons with conventional commercial adsorbent carbons

Yinzhi Zhang, Zhe Lu, Brandon N. Shaffer, M. Mercedes Maroto-Valer*, John M. Andrésen, and Harold H. Schobert

*E-mail: mmm23@psu.edu; Phone no: (814) 863 8265; Fax no: (814) 863 8892
Department of Energy and Geo-Environmental Engineering and The Energy Institute,
The Pennsylvania State University, 405 Academic Activities Building,
University Park, PA 16802

Low-NO_x burner technologies are widely used in coal combustion furnaces in the US to address the implementation of Title IV of the 1990 Clean Air Act Amendments regarding NO_x emissions. However, the concentration of uncombusted coal in the fly ash, generally referred to as fly ash carbon, has also increased, corresponding to lower combustion temperature in the low-NO_x burners [1, 2]. The work presented at the previous 1999, 2000 and 2001 Conferences on Unburned Carbon on Utility Fly Ash focused on the utilization of fly ash carbon as precursor for the generation of activated carbon products [1-3]. However, the unburned carbon in fly ash has gone through a devolatilization process while in the combustor at temperatures above 1200^{o}C. These temperatures are much higher than those conventionally used for devolatization or carbonization of precursors of activated carbons. Therefore, the reactivity of fly ash carbons during the activation process is relatively low, as previously reported [2-3]. Accordingly, during this last year the authors have focused on the development and optimization of a pretreatment process prior to steam activation to improve the reactivity of fly ash carbons.

Experimental procedures

The activation of the fly ash carbons was carried out in an activation furnace that was designed and used by the authors to activate carbons from coal-fired power plant ashes [4]. The authors have demonstrated that a one-step process, that includes simultaneous carbonization and activation, can be employed successfully for these materials [2-4]. This is due to the nature of the unburned carbon, that has already gone through a devolatilization step while in the combustor, and therefore, only requires to be activated. The identified process is now being optimized to design a superior route for the generation of activated carbon materials from carbon in fly ash, that have similar properties to commercial activated carbons. This process involves physical activation with steam of the unburned carbons at temperatures around 850°C for periods of 1-2 hours. The fly ash carbon sample investigated (FA1) was firstly pretreated at 300 to 400^{o}C for 2 to 4 hours, followed by steam activation at 850^{o}C for 1 hour.

Results and discussion

The fly ash carbon from coal-fired power plants can be used as precursor for the production of activated carbons, as demonstrated previously by the authors [3]. As previously reported, the one-step steam activation process can effectively convert fly ash carbons with surface areas typically around 40m^2/g, into activated carbons with surface areas higher than 540m^2/g [3]. However, as the activation time increases, the developing rate of micropore volume decreases, where micropore volumes are highly desired in commercial activated carbons. Therefore, a pretreatment process has been designed and applied to fly ash carbons to improve their reactivity, and therefore, to modify the micropore structure of

the resultant activated carbon. In this study, the samples were pretreated for 2 to 4 hours at 300°C to 400°C prior to 1 hour steam activation at 850°C. For the purpose of comparison, the sample with no pretreatment was also investigated. As for the samples pretreated at 400°C, the activated carbons prepared after pretreatment at 300°C have similar isotherm shapes to that of the sample without pretreatment, but they have much larger adsorbed volume, suggesting a similar microporosity structure, but a higher surface area and total pore volume. However, when the pretreatment time is extended to more than 3 hours, a broader pore size distribution with larger micropores and some mesopores was observed. Raw unburned carbon materials have low surface area and pore volume, where the sample used for this ustudy has a surface area ~115m^2/g [5]. The pretreatment increases the surface area of the resultant activated carbon up to ~60% (from 538m^2/g without pretreatment to 862m^2/g with 2 hour pretreatment at 400°C) compared to that of the sample without pretreatment. In addition, the pretreated samples have similar average pore size to the sample without pretreatment. For extended pretreatment periods (4 hours for 300°C and 3 hours for 400°C), there is no further increase of the surface area, but rather a widening of the existent micropores and an increase of the total pore volumes. For example, for the samples pretreated at 400°C, the extended pretreatment time also decreases the surface area, from 862m^2/g for 2 hr pretreatment to 851m^2/g for 3 hr pretreatment. Therefore, it can be concluded that for the lower pretreatment temperature, the optimum pretreatment time is longer than that of the higher temperature pretreatment (3 hour for 300°C pretreatment vs. 2 hours for 400°C pretreatment).

Concluding remarks

Following previous work conducted to develop activated carbon from fly ash carbons by steam activation, this paper summarizes a parametric study to optimize a pretreatment process. All the different pretreatment conditions studied promote the porosity of resultant activated carbons, where the surface area increases ~11-60%. Furthermore, with increasing pretreatment temperature, both the surface area and pore volume increase for the resultant activated carbon. The optimum pretreatment conditions found during the current reporting period are 400°C and 2 hours, where the resultant activated carbon has a surface area of 862m^2/g, which is comparable to the values reported for commercial activated carbons. Finally, iodine number tests to assess the most suitable commercial applications of the activated fly ash carbons are being conducted at our laboratories, and the results will be reported.

Literature cited

1. Maroto-Valer, M.M., Taulbee, D.N., Hower, J.C., and Schobert, H.H. Proceedings Conference on Unburned Carbon on Utility Fly Ash, 1999, 37
2. Maroto-Valer, M.M., Andrésen, J.M., Morrison, J.L., and Schobert, H.H., Proceedings Conference on Unburned Carbon on Utility Fly Ash, 2000, 21.
3. Maroto-Valer, M.M., Andrésen, J.M., Morrison, J.L., and Schobert, H.H., Proceedings Conference on Unburned Carbon on Utility Fly Ash, 2001, 9.
4. M. M. Maroto-Valer, Y. Zhang, J. M. Andrésen, A. Jones and J. L.Morrison, Prepr. Am. Chem. Soc. Div. Fuel Chem., 2001, 46(1), 316.
5. Maroto-Valer, M.M., Taulbee, D.N., and Hower, J.C. Fuel, 2001, 80, 795.

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